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(54) CURABLE COMPOSITION

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a curable composition which gives a cured product modified in surface properties and reduced in residual tack in a matte state.
SOLUTION: The curable composition comprises a vinyl polymer (particularly a (meth)acrylic polymer) bearing at least one crosslinkable silyl group and having a molecular weight distribution of less than 1.8, and a particle having an average particle size of at least 1 μm and at most 1,000 μm. Preferably, the main chain of the vinyl polymer is one manufactured by a living radical polymerization method (in particular an atom transfer radical polymerization method). Thus, the curable composition which gives a cured product modified in surface properties and reduced in residual tack in a matte state is realized.

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CLAIMS

[Claim(s)]
[Claim 1] The following two components: The vinyl system polymer (I) which has at least one (A) cross-linking functional group, and the hardenability constituent containing a with a (B) mean particle diameter [1 micrometer or more / 1000 micrometer or less] particle (II).
[Claim 2] The hardenability constituent according to claim 1 characterized by containing the vinyl system polymer (I) whose molecular weight distribution is less than 1.8.
[Claim 3] The hardenability constituent according to claim 1 or 2 characterized by containing the vinyl system polymer (I) which is what is manufactured by mainly carrying out the polymerization of the monomer chosen from the group which a principal chain becomes from an acrylic (meta) monomer, an acrylonitrile system monomer, an aromatic series vinyl system monomer, a fluorine content vinyl system monomer, and a silicon content vinyl system monomer.
[Claim 4] A hardenability constituent given in any 1 term of claims 1-3 characterized by a principal chain containing the vinyl system polymer (I) which is an acrylic (meta) polymer.
[Claim 5] A hardenability constituent given in any 1 term of claims 1-3 characterized by a principal chain containing the vinyl system polymer (I) which is an acrylic polymer.
[Claim 6] The hardenability constituent according to claim 5 characterized by a principal chain containing the vinyl system polymer (I) which is an acrylic ester system polymer.
[Claim 7] A hardenability constituent given in any 1 term of claims 1-6 characterized by a cross-linking functional group containing the vinyl system polymer (I) in a principal chain end.
[Claim 8] A hardenability constituent given in any 1 term of claims 1-7 characterized by a cross-linking functional group containing the vinyl system polymer (I) which is a cross-linking silyl radical.
[Claim 9] A hardenability constituent given in any 1 term of claims 1-7 characterized by a cross-linking functional group containing the vinyl system polymer (I) which is an alkenyl radical.
[Claim 10] A hardenability constituent given in any 1 term of claims 1-7 characterized by a cross-linking functional group containing the vinyl system polymer (I) which is a hydroxyl group.
[Claim 11] A hardenability constituent given in any 1 term of claims 1-7 characterized by a cross-linking functional group containing the vinyl system polymer (I) which is an amino group.
[Claim 12] A hardenability constituent given in any 1 term of claims 1-7 characterized by a cross-linking functional group containing the vinyl system polymer (I) which is the radical which has the carbon-carbon double bond of polymerization nature.
[Claim 13] The hardenability constituent according to claim 1 to 7 characterized by a cross-linking functional group containing the vinyl system polymer (I) which is an epoxy group.
[Claim 14] It is a hardenability constituent given in any 1 term among claims 1-13 characterized by containing the vinyl system polymer whose principal chain of a vinyl system polymer (I) is what is manufactured by the living radical polymerization method.
[Claim 15] The hardenability constituent according to claim 14 characterized by a living radical polymerization containing the vinyl system polymer which is an atomic migration radical polymerization.
[Claim 16] The hardenability constituent according to claim 15 with which an atomic migration radical polymerization is characterized by containing the vinyl system polymer with which the

complex chosen from the transition metal complex which uses the 7th group of the periodic table, eight groups, nine groups, ten groups, or 11 group element as a central metal is made into a catalyst.
[Claim 17] The hardenability constituent according to claim 16 characterized by containing the vinyl system polymer which is a complex with which the metal complex made into a catalyst is chosen from the group which it becomes from the complex of copper, nickel, a ruthenium, or iron.
[Claim 18] The hardenability constituent according to claim 17 characterized by containing the vinyl system polymer whose metal complex made into a catalyst is a copper complex.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the vinyl system polymer (I) which has at least one cross-linking silyl radical, and the hardenability constituent containing a with a 1-micrometer or more mean particle diameter [1000 micrometer or less] particle (II).
[0002]
[Description of the Prior Art] What has a functional group at a functional group, especially the end with the polymer of the vinyl system obtained according to a radical polymerization by one side of the polymer obtained by ionic polymerization or condensation polymerization is hardly put in practical use yet. Also in the vinyl system polymer, the acrylic (meta) polymer has the property which is not acquired in polyether system polymers, such as high weatherability and transparency, a hydrocarbon system polymer, or a polyester system polymer, and what has an alkenyl radical and a cross-linking silyl radical in a side chain is used for the coating of high weatherability etc. On the other hand, polymerization control of an acrylic polymer is not easy because of the side reaction, and installation of the functional group to an end etc. is very difficult.
[0003] If the vinyl system polymer which has an alkenyl radical at the chain end can be obtained by the simple approach, the hardened material which excelled [side chain] in hardened material physical properties as compared with what has a cross-linking radical can be obtained. Therefore, although the manufacturing method has been examined by the researcher of the former many, it is not easy to manufacture them industrially. For example, the synthesis method of the acrylic polymer which has an alkenyl radical at the end (meta) which uses alkenyl radical content disulfide as a chain transfer agent is indicated by JP,1-247403,A and JP,5-255415,A.
[0004] In JP,5-262808,A, the vinyl system polymer which has hydroxyl in both ends is compounded using the disulfide which has hydroxyl, and the synthesis method of the acrylic polymer which has an alkenyl radical at the end (meta) is further indicated using the reactivity of hydroxyl.
[0005] In JP,5-211922,A, the vinyl system polymer which has hydroxyl in both ends is compounded using the polysulfide which has hydroxyl, and the synthesis method of the acrylic polymer which has a silyl radical at the end (meta) is further indicated using the reactivity of hydroxyl.
[0006] By these approaches, it is difficult to introduce a functional group into both ends certainly, and the hardened material which has a satisfactory property cannot be obtained. In order to introduce a functional group into both ends certainly, a chain transfer agent must be used in large quantities, and it is a production process top problem. Moreover, since the usual radical polymerization is used by these approaches, the molecular weight of the polymer obtained and control of molecular weight distribution (ratio of number average molecular weight and number average molecular weight) are difficult.
[0007] Artificers have invented many to such a Prior art about the vinyl system polymer which has cross-linking functional groups various until now at the end, its manufacturing method, a hardenability constituent, and an application (see JP,11-080249,A, JP,11-080250,A, JP,11-

005815,A, JP,11-116617,A, JP,11-116606,A, JP,11-080571,A, JP,11-080570,A, JP,11-130931,A, JP,11-100433,A, JP,11-116783,A, JP,9-272714,A, JP,9-272715,A, etc.).
[0008] For example, the silicon content radical which can construct a bridge by having the hydroxyl group or hydrolysis nature machine combined with the silicon atom, and forming siloxane association with hygroscopic moisture etc. also in a room temperature The hardened material obtained from the vinyl system polymer which has (it is also hereafter called a "cross-linking silyl radical"), or its constituent Although it excels in thermal resistance or weatherability and especially limitation is not carried out, sealing materials, such as a structural elastic sealing compound sealant and a sealing material for multiple glass, Electrical insulation materials, such as electrical and electric equipment and electronic-parts ingredients, such as a solar-battery rear-face sealing agent, and pre-insulation an electric wire, material for cables, A binder, adhesives, elastic adhesives, a coating, powder coatings, a coating material, foam, It is available for various applications, such as seals, such as the potting agent for electric electrons, a film, a gasket, a casting ingredient, various molding materials and wired glass, and rust proofing and the sealing agent for waterproofing of a glass laminate end face (cutting section), autoparts, and electrical machinery components, various machine parts.
[0009] Also in the aforementioned application, generally the joint and clearance between [various] members are filled up with a sealing material, especially a general structural sealant, etc., and it is used in order to give a watertight and an airtight. Therefore, since the flattery nature to the use part over a long period of time is very important, being a low modulus, high elongation, and high intensity, and holding those physical properties as physical properties of a hardened material, over a long period of time is called for. Moreover, by one side, hypoviscosity is demanded as a hardenability constituent (compound) in consideration of workability in these construction.
[0010] the hardened material of the hardenability constituent which made it the raw material when giant-molecule quantification of the vinyl system polymer was carried out — a low modulus and high elongation — although it can high-intensity-ize, the viscosity of this compound becomes high and the workability at the time of construction worsens. On the contrary, if a vinyl system polymer is hypoviscosity-ized, although workability becomes good, the machine physical properties of a hardened material will fall (a high modulus, low elongation, low-strength-izing). Then, in order to solve this technical problem, a phthalic-acid system plasticizer like the phthalic ester which does not have a functional group, a polyether system plasticizer, etc. are usually used.
[0011]
[Problem(s) to be Solved by the Invention] However, if such a plasticizer is blended so much, in the hardened material which stiffened the compound, a plasticizer will pass, bleeding (it is also called shift and oil bleeding) will be carried out to a hardened material front face by the time, and problems, such as smeariness, will be produced. Furthermore, the problem of causing the fall of the surface contamination after the contamination to the circumference and paint of a hardened material (sealant etc.), an adhesive fall, the hardness of a hardened material, elongation, etc. by that is also produced.
[0012] Moreover, since the polymer which has the hydrolysis nature silicon radical which two adding-water nature resolvability radicals per silicon atom come to join together was used in many cases, the vinyl system polymer which has such a cross-linking silyl radical To take [when you need the very quick cure rates in the case of using it at the application etc. and low temperature of adhesives etc. especially, the cure rate is not enough, and] out the flexibility after hardening Crosslinking density needed to be reduced, therefore since crossfinking density was not enough, there was a problem that there was stickiness (surface tuck).
[0013] Then, the vinyl system polymer with which this invention has at least one cross-linking silyl radical, And it is the hardenability constituent which uses as a principal component the polyether system polymer which has 1.2 or less cross-linking silyl radicals on the average. Have good workability by hypoviscosity and contamination (coating stain resistance is included) of a hardened material is reduced by controlling the bleeding of the plasticizer to the front face of the hardened material which stiffened the hardenability constituent. Moreover, the hardened

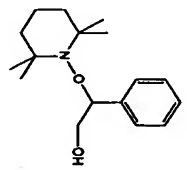
material is a low modulus and high elongation, and the machine physical properties are maintained over a long period of time, and it is in offering the constituent which has a still better adhesive property, good alkyd paintwork, and a high gel molar fraction.
[0014]
[Means for Solving the Problem] this invention person etc. completed a header and this invention for solving the above-mentioned technical problem by using the vinyl system polymer which has at least one cross-linking silyl radical, and the hardenability constituent which uses a with a 1-micrometer or more mean particle diameter [1000 micrometer or less] particle as a principal component, as a result of inquiring wholeheartedly, in order to solve such a problem.
[0015] That is, this invention relates to the vinyl system polymer (I) which has at least one cross-linking silyl radical, and the hardenability constituent containing a with a 1-micrometer or more mean particle diameter [1000 micrometer or less] particle (II).
[0016] Although especially a vinyl system polymer (I) is not limited, it is desirable that the value of the ratio (Mw/Mn) of the weight average molecular weight (Mw) measured with gel permeation chromatography and number average molecular weight (Mn) is less than 1.8.
[0017] Although especially the principal chain of a vinyl system polymer (I) is not limited, furthermore, an acrylic (meta) monomer, It is desirable to mainly carry out the polymerization of the monomer chosen from the group which consists of an acrylonitrile system monomer, an aromatic series vinyl system monomer, a fluorine content vinyl system monomer, and a silicon content vinyl system monomer, and to be manufactured. more -- desirable — an acrylic (meta) monomer — further — desirable -- an acrylic monomer — It is an acrylic ester system monomer more preferably, and it is most desirable to carry out a polymerization and to be manufactured using a butyl acrylate system monomer, from the point that physical properties, such as hypoviscosity of a compound, a low modulus of a hardened material, high elongation, weatherability, and thermal resistance, are required in the application of general ********. Moreover, it is desirable to carry out a polymerization and to be manufactured using an ethyl-acrylate system monomer, in the application of the circumference of the engine of the automobile of which oilproof, thermal resistance, high intensity, etc. are required, a machine, etc., by one side, and it is more desirable to copolymerize an ethyl-acrylate system monomer mainly using an acrylic-acid 2-methoxy ethyl system monomer and a butyl acrylate system monomer, and to be further, manufactured from balance, such as cold resistance. It is possible to change the ratio of a monomer to copolymerize in consideration of physical properties, such as oilproof and a low-temperature property.
[0018] Moreover, although limitation is not carried out, as for the principal chain of this vinyl system polymer (I), being manufactured according to a living radical polymerization is desirable, and it is more desirable that it is an atomic migration radical polymerization. Furthermore, although limitation is not carried out, as for an atomic migration radical polymerization, it is desirable to make into a catalyst the complex chosen from the transition metal complex which uses the 7th group of the periodic table, eight groups, nine groups, ten groups, or 11 group element as a central metal, it is more desirable, and especially a copper complex is desirable [a radical polymerization] especially. [of the complex chosen from the group which consists of a complex of copper, nickel, a ruthenium, or iron]
[0019] The location of the cross-linking silyl radical of a vinyl system polymer (I) has a desirable end, although limitation is not carried out. In addition, although you may have the same functional group as the interior of a principal chain, when asking for rubber elasticity the hardened material made to construct a bridge, it is desirable to have a functional group only at the end.
[0020] Although especially the number of the cross-linking functional groups of a vinyl system polymer (I) is not limited, in order to obtain a hardened material with more high cross-linking, it is desirable to have one or more pieces on the average, and it is 1.2 or more pieces [3.5 or less] still more preferably 4.0 or less [1.1 or more] more preferably. Although especially limitation is not carried out, as for the mean particle diameter of a with a 1-micrometer or more mean particle diameter [of this invention / 1000 micrometer or less] particle (II), it is desirable that it is 500 micrometers or less from points, such as workability and the machine physical properties of a hardened material.

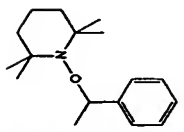
[0021]
[Embodiment of the Invention] This invention relates to a hardenability constituent. Furthermore, it is related with the vinyl system polymer (I) which has following at least one 2 component:cross-linking functional group, and the hardenability constituent containing a with a 1-micrometer or more mean particle diameter [1000 micrometer or less] particle (II) in detail. Below, the hardenability constituent of this invention is explained in full detail.
< <vinyl system polymer> > <principal chain> this invention persons The vinyl system polymer which has cross-linking functional groups various until now at the polymer end, The manufacturing method, a hardenability constituent, And it is related with an application. Much invention The line came. JP,11-080249,A, JP,11-080250,A, JP,11-005815,A, JP,11-116617,A, JP,11-116606,A, JP,11-080571,A, JP,11-080570,A, JP,11-130931,A, and JP,11-100433,A — Refer to JP,11-116783,A, JP,9-272714,A, JP,9-272715,A, etc. Although not limited especially as a vinyl system polymer (I) of this invention, all the polymers indicated by invention illustrated above can be used suitably.
[0022] It is not limited especially as a vinyl system monomer which constitutes the principal chain of the vinyl system polymer of this invention, but various kinds of things can be used. If it illustrates, an acrylic acid (meta), a methyl acrylate (meta), An ethyl acrylate, acrylic-acid (meta)-n-propyl, acrylic-acid (meta) isopropyl, (Meta) Acrylic-acid-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic-acid-tert-butyl, acrylic-acid (meta)-n-pentyl, (Meta) Acrylic-acid-n-hexyl, acrylic-acid (meta) cyclohexyl, (Meta) Acrylic-acid-n-heptyl, acrylic-acid (meta)-n-octyl, (Meta) 2-ethylhexyl acrylate, acrylic-acid (meta) nonyl, (Meta) Acrylic-acid DESHIRU, acrylic-acid (meta) dodecyl, acrylic-acid (meta) phenyl, (Meta) Acrylic-acid tolyl, acrylic-acid (meta) benzyl, acrylic-acid (meta)-2-methoxy ethyl, (Meta) Acrylic-acid-3-methoxy butyl, acrylic-acid (meta)-2-hydroxyethyl, (Meta) 2-hydroxypropyl acrylate, acrylic-acid (meta) stearyl, (Meta) Metaglycidyl acrylate, acrylic-acid (meta) 2-aminoethyl, (Meta) gamma-(methacryloyl oxypropyl) trimethoxysilane, the ethyleneoxide addition product of an acrylic acid (meta), Acrylic-acid trifluoromethyl methyl, an acrylic-acid (meta) 2-trifluoro methylethyl, (Meta) Acrylic-acid perfluoro ethyl methyl, acrylic-acid (meta) 2-perfluoro ethyl ethyl, (Meta) Acrylic-acid perfluoro ethyl perfluoro BUCHIRUMECHIRU, (Meta) Acrylic-acid 2-perfluoro ethyl-2-perfluoro butyl ethyl, (Meta) Acrylic-acid perfluoro ethyl, acrylic-acid (meta) perfluoro methyl, (Meta) Acrylic-acid JIPA fluoro methyl methyl, an acrylic acid (meta) 2, 2-JIPA fluoro methylethyl, (Meta) Acrylic-acid perfluoro methyl perfluoro ECHIRUMECHIRU, (Meta) Acrylic-acid 2-perfluoro methyl-2-perfluoro ethyl ethyl, (Meta) Acrylic-acid 2-perfluoro hexyl methyl, acrylic-acid (meta) 2-perfluoro hexyl ethyl, (Meta) Acrylic-acid 2-perfluoro DESHIRU methyl, acrylic-acid (meta) 2-perfluoro DESHIRU ethyl, (Meta) Acrylic (meta) monomers, such as acrylic-acid 2-perfluoro hexadecyl methyl and acrylic-acid (meta) 2-perfluoro hexadecyl ethyl; Styrene, (Meta) Aromatic series vinyl system monomers, such as vinyltoluene, alpha methyl styrene, KURORU styrene, a styrene sulfonic acid, and its salt; Perfluoro ethylene, Fluorine content vinyl system monomers, such as a perfluoro propylene and vinylidene fluoride; Vinyltrimetoxysilane, Silicon content vinyl system monomers, such as vinyltriethoxysilane; A maleic anhydride, Monoalkyl ester and dialkyl ester of a maleic acid and a maleic acid; A fumaric acid, Monoalkyl ester and dialkyl ester of a fumaric acid; Maleimide, Methyl maleimide, ethylmaleimide, propyl maleimide, butylmaleimide, Hexyl maleimide, octyl maleimide, dodecyl maleimide, stearyl maleimide, Maleimide system monomers, such as phenyl maleimide and cyclohexyl maleimide; Acrylonitrile, Acrylonitrile system monomers, such as a methacrylonitrile; Acrylamide, Amide group content vinyl system monomers, such as methacrylamide; Vinyl acetate, Conjugated dienes, such as alkenes; butadienes, such as vinyl ester; ethylene, such as propionic-acid vinyl, vinyl pivalate, benzoic-acid vinyl, and cinnamic acid vinyl, and a propylene, and an isoprene; a vinyl chloride, a vinylidene chloride, an allyl chloride, allyl alcohol, etc. are mentioned. These may be used independently, and even if it carries out copolymerization of the plurality, they are not cared about.
[0023] It is desirable that it is what is manufactured by mainly carrying out the polymerization of at least one monomer chosen from the group which the principal chain of a vinyl system polymer becomes from an acrylic (meta) monomer, an acrylonitrile system monomer, an aromatic series vinyl system monomer, a fluorine content vinyl system monomer, and a silicon content vinyl

system monomer, here — "— mainly — " — it means more than 50 mol % and that it is the above-mentioned monomer 70% or more of preferably among the monomeric units which constitute a vinyl system polymer.
[0024] Especially, the styrene system monomer from physical properties etc. and (meta) acrylic-acid system monomer of a product are desirable. More preferably, it is an acrylic ester monomer and a methacrylic ester monomer, and is an acrylic ester monomer especially preferably. The point that physical properties, such as hypoviscosity of a compound, a low modulus of a hardened material, high elongation, weatherability, and thermal resistance, are required in the application of general ******** to a butyl acrylate system monomer is still more desirable. The copolymer mainly concerned with the ethyl acrylate on the other hand in the application as which oilproof [, such as an automotive application,] etc. is required is still more desirable. It can also transpose a part of ethyl acrylate to butyl acrylate in order to raise that low-temperature property, since it has the inclination to be a little inferior to a low-temperature property (cold resistance), although the polymer mainly concerned with this ethyl acrylate is excellent in oilproof. However, since it follows on increasing the ratio of butyl acrylate and oilproof [the / good] is spoiled, as for the ratio, for the application of which oilproof is required, it is desirable to carry out to 40% or less, and it is more desirable to make it to 30 more% or less. Moreover, in order to improve a low-temperature property etc., without spoiling oilproof, it is also desirable to use acrylic-acid 2-methoxy ethyl, acrylic-acid 2-ethoxyethyl, etc. by which oxygen was introduced into the alkyl group of a side chain. However, since it is in the inclination for thermal resistance to be inferior with the installation of an alkoxy group which has ether linkage in a side chain, when thermal resistance is required, it is desirable [the ratio] to make it to 40% or less. It is possible to obtain the polymer which the ratio was changed in consideration of physical properties, such as oilproof [which is needed], and thermal resistance, a low-temperature property, according to various applications or the purpose demanded, and was suitable. For example, as an example which is excellent in physical-properties balance, such as oilproof, and thermal resistance, a low-temperature property, although limitation is not carried out, the copolymer of an ethyl acrylate / butyl acrylate / acrylic-acid 2-methoxy ethyl (it is 40-50/30 / 20 at a weight ratio) is mentioned. [20-30] [30-20]
[0025] In this invention, it is desirable other monomers, copolymerization, and that may carry out block copolymerization further and these desirable monomers are contained 40% by the weight ratio in these desirable monomers in that case. In addition, an acrylic acid (meta) expresses an acrylic acid and/, or a methacrylic acid with the above-mentioned transcription.
[0026] Although especially the molecular weight distribution of the vinyl system polymer of this invention, i.e., the ratio of the weight average molecular weight (Mw) and number average molecular weight (Mn) which were measured with gel permeation chromatography, (Mw/Mn) are not limited, it is less than 1.8 preferably, is 1.7 or less more preferably, is 1.6 or less still more preferably, is 1.5 or less still more preferably, is 1.4 or less especially preferably, and is 1.3 or less most preferably. In the GPC measurement by this invention, using chloroform as a mobile phase, a polystyrene gel column can perform measurement and number average molecular weight etc. can usually be calculated by polystyrene conversion.
[0027] Although especially a limit does not have the number average molecular weight of the vinyl system polymer in this invention, when it measures with gel permeation chromatography, the range of 500-1,000,000 is desirable, 1,000-100,000 are more desirable, and 5,000-50,000 are still more desirable.
Although limitation is not carried out, the synthesis method of the vinyl system polymer in <synthesis method of principal chain> this invention has a desirable control radical polymerization, is more desirable, and is desirable. [of especially an atomic migration radical polymerization] [of a living radical polymerization] These are explained below.
A control radical polymerization radical polymerization method can be classified into "the general radical polymerization method" to which copolymerization of the monomer which has a specific functional group, and the vinyl system monomer is only carried out, and the "control radical polymerization method" which can introduce a specific functional group into the location controlled [end], using an azo system compound, a peroxide, etc. as a polymerization initiator.

[0028] Although "a general radical polymerization method" is a simple approach, since the monomer which has a specific functional group by this approach is not introduced into a probable polymer, when it is going to obtain a polymer with the high rate of organic-functions-izing, it is necessary to use this monomer quite in large quantities, and there is a trouble that the rate of a polymer that this specific functional group is not introduced becomes large, by little use conversely. Moreover, since it is a free radical polymerization, the trouble that only a large polymer with high viscosity is obtained also has molecular weight distribution.
[0029] A "control radical polymerization method" can be classified into the "chain transfer agent method" the vinyl system polymer which has a functional group at the end is obtained, and the "living radical polymerization method" the polymer of the molecular weight as a design is mostly obtained by growing without a polymerization growth end causing termination reaction etc., by performing a polymerization using the chain transfer agent which has a further specific functional group.
[0030] Although a "chain transfer agent method" can obtain a polymer with the high rate of organic-functions-izing, the chain transfer agent which has quite a lot of specific functional groups to an initiator is required for it, and it has a problem on the financial side also including processing. Moreover, like the above-mentioned "general radical polymerization method", since it is a free radical polymerization, the trouble that it is large and only a polymer with high viscosity is obtained also has molecular weight distribution.
[0031] While termination reaction cannot occur easily and the narrow (Mw/Mn is 1.1 to about 1.5) polymer of molecular weight distribution is obtained though it is the radical polymerization made difficult [control] since the termination reaction a "living radical polymerization method" has a high rate of polymerization, and according to coupling of radicals etc. tends to occur unlike these polymerization methods, molecular weight is freely controllable with the preparation ratio of a monomer and an initiator.
[0032] Therefore, a "living radical polymerization method" has narrow molecular weight distribution, and is more desirable as the manufacture approach of a vinyl system polymer of having the above-mentioned specific functional group for the monomer which can obtain a polymer with low viscosity upwards and has a specific functional group since [of a polymer] it can introduce into the location of arbitration mostly.
[0033] In addition, although living polymerization means the polymerization to which an end always continues having activity and the chain grows in the narrow sense, the pseudo-living polymerization which grows while that by which the end was inactivated, and the activated thing are generally in an equilibrium state is also contained. The definition in this invention is also the latter.
[0034] As for the "living radical polymerization method", research is positively made into groups various in recent years. As the example, for example A journal OBU American chemical society (J. Am.Chem.Soc.), 1994, 116 volumes, the thing using a cobalt porphyrin complex as shown in 7943 pages, Macro leakage-at-bulb KYURUZU (Macromolecules), 1994, The thing using radical scavengers, such as 27 volumes and a nitroxide compound as shown in 7228 pages, "The atomic migration radical polymerization" (Atom Transfer Radical Polymerization:ATRP) etc. which makes an organic halogenide etc. an initiator and makes a transition metal complex a catalyst is raised.
[0035] Also in a "living radical polymerization method", an organic halogenide or a halogenation sulfonyl compound An initiator, "The atomic migration radical polymerization method" which carries out the polymerization of the vinyl system monomer by making a transition metal complex into a catalyst As the manufacture approach of a vinyl system polymer of in addition to the description of the above-mentioned "living radical polymerization method" having a halogen comparatively advantageous to a functional-group conversion reaction etc. at the end, and having a specific functional group from the degree of freedom of a design of an initiator or a catalyst being large, it is still more desirable. As this atomic migration radical polymerization method, Matyjaszewski et al. [for example,], Journal OBU American chemical society (J. Am.Chem.Soc.) 1995, 117 volumes, 5614 pages, macro leakage-at-bulb KYURUZU (Macromolecules) 1995, 28 volumes, 7901 pages, Science (Science) 1996, 272 volumes, 866 pages, WO 96/No. 30421 official report, WO 97/No. 18247 official report, WO 98/No. 01480

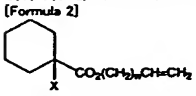
official report, WO 98/No. 40415 official report, or Sawamoto et al., 28 volumes, 1721 pages, JP,9-208616,A, JP,8-41117,A, etc. will be mentioned in macro leakage-at-bulb KYURUZU (Macromolecules) 1995.
[0036] In this invention, although which approach is used among these living radical polymerizations does not have especially constraint, an atomic migration radical polymerization method is desirable.
[0037] Although the living radical polymerization is explained below at the detail, the polymerization using 1 of the control radical polymerizations which can be used for manufacture of the vinyl system polymer later explained before that, and a chain transfer agent is explained. Especially as a radical polymerization using a chain transfer agent (telomer), although not limited, the following two approaches are illustrated as an approach of obtaining a vinyl system polymer with the end structure suitable for this invention.
[0038] They are the approach of obtaining the polymer of a halogen end, using halogenated hydrocarbon as shown in JP,4-132706,A as a chain transfer agent, and a method of obtaining the polymer of a hydroxyl-group end, using a hydroxyl-group content mercaptan or a hydroxyl-group content polysulfide as shown in JP,61-271306,A, JP,2594402,B, and JP,54-47782,A etc. as a chain transfer agent.
[0039] Below, a living radical polymerization is explained.
[0040] Among those, the approach using radical scavengers, such as a nitroxide compound, is explained first. Generally in this polymerization, a stable nit ROKISHI free radical (= N-O-) is used as a radical capping agent. As such compounds, although limitation is not carried out, the nit ROKISHI free radical from annular hydroxy amines, such as a 2, 2, 6, and 6-permutation-1-piperidinyloxy radical and a 2, 2, 5, and 5-permutation-1-pyrrolidinyl oxy-radical, is desirable. As a substituent, a with a carbon numbers [, such as a methyl group and an ethyl group,] of four or less alkyl group is suitable. As a concrete nit ROKISHI free radical compound Although limitation is not carried out, 2, 2, 6, a 6-tetramethyl-1-piperidinyloxy radical (TEMPO), A 2, 2, 6, and 6-tetraethyl-1-piperidinyloxy radical, A 2, 2, 6, and 6-tetramethyl-4-oxo--1-piperidinyloxy radical, 2, 2, 5, and 5-tetramethyl-1-pyrrolidinyl oxy-radical, 1, 1 and 3, and 3-tetramethyl-2-ISOINDORI nil oxy-radical, N, and N-G tert butylamine oxy-radical etc. is mentioned. Instead of a nit ROKISHI free radical, a free radical with a stable galvinoxyl (galvinoxyl) free radical etc. may be used.
[0041] The above-mentioned radical capping agent is used together with a radical generating agent. It is thought that the resultant of a radical capping agent and a radical generating agent serves as a polymerization initiator, and the polymerization of an addition polymerization nature monomer advances. Although especially both concomitant use rate is not limited, 0.1-10 mols of radical initiators are suitable to radical capping agent 1 Mol.
[0042] As a radical generating agent, although various compounds can be used, the peroxide which may generate a radical is desirable under polymerization temperature conditions. As this peroxide, although limitation is not carried out, there are alkyls perester, such as peroxy carbonates, such as diallkyl peroxide, such as diacyl peroxide, such as benzoyl peroxide and lauroyl peroxide, JIKUMIRU peroxide, and G t-butyl peroxide, diisopropyl peroxi dicarbonate, and bis(4-t-butyl cyclohexyl) peroxi dicarbonate, t-butyl peroxyoctoate, and t-butyl peroxybenzoate, etc. Especially benzoyl peroxide is desirable. Furthermore, radical generating agents, such as a radical generating nature azo compound like azobisisobutyronitril, can also be used instead of peroxide.
[0043] Macromolecules An alkoxy amine compound as shown in the following figure may be used as an initiator instead of using together a radical capping agent and a radical generating agent as reported by 1995, 28, and P.2993.
[0044]
[Formula 1]



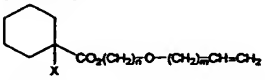


If what has functional groups, such as a hydroxyl group as it shown in the above figure, is used when using an alkoxy amine compound as an initiator, the polymer which has a functional group at the end will be obtained. If this is used for the approach of this invention, the polymer which has a functional group at the end will be obtained.
[0045] Although polymerization conditions, such as the monomer and solvent which are used by the polymerization using radical scavengers, such as the above-mentioned nitroxide compound, and polymerization temperature, are not limited, they are the same as that of what is used about the atomic migration radical polymerization explained below, and are not cared about.
The more desirable atomic migration radical polymerization method as an atomic migration radical polymerization, next a living radical polymerization of this invention is explained.
[0046] In this atomic migration radical polymerization, an organic halogenide especially the organic halogenide (for example, the carbonyl compound which has a halogen in an alpha position and the compound which has a halogen in the benzylic position) which has reactant high carbon-halogen association, or a halogenation sulfonyl compound is used as an initiator. it illustrates concretely — if it becomes — C6H5-CH2X, C6H5-C(H) (X) CH3, and C6H5-C (X) (CH3) — two (however, the inside of the upper chemical formula, C6 H 5 a phenyl group and X chlorine, a bromine, or iodine) —
R1-C(H) (X)-CO two R2, R1-C(CH3) (X)-CO two R2, R1-C(H) (X)-C(O) R2, R1-C(CH3) (X)-C (O) R2 (among a formula), For R1 and R2, a hydrogen atom or the alkyl group of carbon numbers 1-20, an aryl group or an aralkyl radical, and X are chlorine, a bromine, or iodine.
R1-C6H4-SO2X (for the inside of a formula and R1, a hydrogen atom or the alkyl group of carbon numbers 1-20, an aryl group or an aralkyl radical, and X are chlorine, a bromine, or iodine) etc. is mentioned.
[0047] The organic halogenide or halogenation sulfonyl compound which has functional groups other than the functional group which starts a polymerization as an initiator of an atomic migration radical polymerization can also be used. In such a case, the vinyl system polymer which has a functional group at one principal chain end, and has the growth end structure of an atomic migration radical polymerization at the principal chain end of another side is manufactured. As such a functional group, an alkenyl radical, a cross-linking silyl radical, hydroxyl, an epoxy group, the amino group, an amide group, etc. are mentioned.
[0048] What has the structure which it is not limited as an organic halogenide which has an

alkenyl radical, for example, is shown in a general formula (1) is illustrated.
R4R5C(X)-R6-R7-C(R3)=CH2 (1)
the inside of a formula, and R3 — hydrogen or a methyl group, and R4 and R5 — hydrogen — The univalent alkyl group of carbon numbers 1-20, an aryl group, an aralkyl radical or the thing mutually connected in the other end, and R6 [or] - X in which C(O) O- (ester group), -C(O)- (keto radical) or o-, m-, p-phenylene group, and R7 may include one or more ether linkage by direct coupling or the divalent organic radical of carbon numbers 1-20 is chlorine, a bromine, or iodine.
As an example of substituents R4 and R5, hydrogen, a methyl group, an ethyl group, n-propyl group, an isopropyl group, butyl, a pentyl radical, a hexyl group, etc. are mentioned. R4 and R5 may be connected in the other end, and they may form the annular frame.
[0049] As an example of an organic halogenide of having the alkenyl radical shown by the general formula (1) XCH2C(O) O(CH2) nCH=CH2, Hthree cc(H) (X) C(O) O(CH2) nCH=CH2, 2(H3C) C(X) C(O) O(CH2) nCH=CH2, CH3CH2C(H) (X) C(O) O(CH2) nCH=CH2, [0050]
[Formula 2]



(Setting at each above-mentioned ceremony, for X, chlorine, a bromine or iodine, and n are the integer of 0-20)
XCH2C (O) O nO (CH2) mCH=CH2, H3cc (CH2) (H) (X) C(O) O(CH2) nO(CH2) mCH=CH2, 2 (H3C) C(X) C(O) O(CH2) nO(CH2) mCH=CH2, CH3CH2C(H) (X) C(O) O(CH2) nO(CH2) mCH=CH2, [0051]
[Formula 3]



(Setting at each above-mentioned ceremony, for chlorine, a bromine or iodine, and n, the integer of 1-20 and m are [X] the integer of 0-20)
o, m, p-XCH2-C6H4-(CH2) n-CH=CH2, o and m, p-CH3C(H) (X)-C6H4-(CH2) n-CH=CH2, o and m, and p-CH3 — CH2C(H) (X)-C6H4-(CH2) n-CH=CH2 (each above-mentioned formula — setting — X — chlorine --), A bromine or iodine, and n are the integer of 0-20.
o, m, p-XCH2-C6H4- n-O- (CH2) (CH2) m-CH=CH2, o and m, and p-CH3 — C(H) (X)-C6H4-(CH2) n-O-(CH2) m-CH=CH2, o and m, and p-CH3CH2 — C(H) (X)-C6H4-(CH2) n-O-(CH2) mCH=CH2 (in each above-mentioned formula), For chlorine, a bromine or iodine, and n, the integer of 1-20 and m are [X] the integer of 0-20.
o, m, and p-XCH2-C6H4-O- (CH2) n-CH=CH2, o and m, and p-CH3 — C(H) (X)-C6H4-O-(CH2) n-CH=CH2, o and m, and p-CH3CH2 — C(H) (X)-C6H4-O-(CH2) n-CH=CH2 (each above-mentioned formula — setting — X — chlorine, a bromine, or iodine --), n is the integer of 0-20.
o, m, and p-XCH2-C6H4-O- n-O- (CH2) m-CH=CH2, o and m, p-CH3C (CH2) (H) — (X)-C6H4-O-(CH2) n-O-(CH2) m-CH=CH2, o and m, and p-CH3CH2C — (H) (X)-C6H4-O-(CH2) n-O-(CH2) — m-CH=CH — two (in each above-mentioned formula) For chlorine, a bromine or iodine, and n, the integer of 1-20 and m are [X] the integer of 0-20.
The compound further shown by the general formula (2) as an organic halogenide which has an alkenyl radical is mentioned.
H2C=C(R3)-R7-C(R4)(X)-R8-R5 (2)
(the inside of a formula, and R3, R4, R5, R7 and X — the above — the same — R8 — direct coupling, -C(O) O- (ester group), and - C(O)- (keto radical) or o-, m-, and p-phenylene group

are expressed)
Although R7 is direct coupling or the divalent organic radical (one or more ether linkage may be included) of carbon numbers 1-20, when it is direct coupling, the vinyl group has combined with the carbon which has combined the halogen, and it is an allyl halide ghost. In this case, since carbon-halogen association is activated by the contiguity vinyl group, there may not not necessarily be need of having C(O) O set, a phenylene group, etc. as R8, and may be direct coupling. When R7 is not direct coupling, in order to activate carbon-halogen association, as R8, O sets, a C(O) C (O) radical, and a phenylene group are desirable.
[0052] If the compound of a general formula (2) is illustrated concretely, CH2=CHCH2X, CH2=C (CH3) CH2X, CH2=CHC (H) (X) CH3, CH2=C C (CH3) (H) (X) CH3, CH2=CHC (X) (CH3) 2, CH2=CHC(H) (X) C2H5, CH2=CHC(H) (X) CH (CH3)2, CH2=CHC(H) (X) C6H5, CH2=CHC(H) (X) CH2C6H5, CH2=CHCH2C(H) (X)-CO2R, CH2=CH(CH2)2C(H) (X)-CO2R, CH2=CH(CH2)3C(H) (X)-CO2R, CH2=CH(CH2)8C(H) (X)-CO2R, CH2=CHCH2C(H) (X)-C6H5, CH2=CH(CH2)2C(H) (X)-C6H5, and CH2=CH(CH2)3C(H) (X)-C6H5 (each above-mentioned formula — setting — X — chlorine and a bromine --), Or iodine and R can mention the alkyl group of carbon numbers 1-20, an aryl group, an aralkyl radical, etc.
[0053] If the example of a halogenation sulfonyl compound of having an alkenyl radical is given, they will be o-, m-, p-CH2=CH-(CH2) n-C6H4-SO2X, o-, m-, p-CH2=CH-(CH2) n-O-C6H4-SO2X, etc. (setting at each above-mentioned ceremony, for X, chlorine, a bromine or iodine, and n are the integer of 0-20).
[0054] What has the structure which it is not limited especially as an organic halogenide which has the above-mentioned cross-linking silyl radical, for example, is shown in a general formula (3) is illustrated.
R4R5C(X)-R8-R7-C(H)(R3)CH2-[Si(R9)2-b(Y)bO]m-Si(R10)3-a(Y)a (3)
the inside of a formula, and R3, R4, R5, R8, R7 and X — the above — the same — R9 and R10 All The alkyl group of carbon numbers 1-20, an aryl group, an aralkyl radical, Or (R') 3SiO - (R' is the univalent hydrocarbon group of carbon numbers 1-20) three R' — being the same — differing — **** — when the Tori ORGANO siloxy radical shown is shown and R9 or two or more R 10 exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolysis nature machine and two or more Y exists, they may be the same and may differ. a shows 0, 1, 2, or 3, and b shows 0, 1, or 2. m is the integer of 0-19. However, it shall satisfy that it is a+mb>=1.
If the compound of a general formula (3) is illustrated concretely XCH2C (O) O nSi (CH2) 3, CH3C (OCH3) (H) (X) C (O) O nSi (CH2) 3, (OCH3) 2C (CH3) (X) C (O) O nSi (CH2) (OCH3) 3, XCH2C(O) O(CH2) nSi (CH3) (OCH3)2, CH3C(H) (X) C(O) O(CH2) nSi (CH3) (OCH3)2, 2(CH3) C (X) C(O) O(CH2) nSi2 (in each above-mentioned formula) (CH3) (OCH3), For X, chlorine, a bromine, iodine, and n are the integer of 0-20,
XCH2C (O) O nO (CH2) mSi (CH2) 3 H3cc (OCH3) (H) (X) C (O) O nO (CH2) mSi (CH2) 3, (OCH3) 2C (H3C) (X) C (O) O nO (CH2) mSi (CH2) 3, CH3CH2C (OCH3) (H) (X) C (O) O nO (CH2) mSi (CH2) 3, XCH2C (OCH3) (O) O nO (CH2) mSi (CH2) (CH3) 2 H3cc (OCH3) (H) (X) C (O) O nO (CH2) m-Si (CH2) (CH3) 2, 2(H3C) C(X) C(O) O(CH2) nO(CH2) m-Si (CH3) (OCH3)2, and CH3CH2C(H) (X) C(O) O(CH2) nO(CH2) m-Si (OCH3) (CH3)2 (each above-mentioned formula — setting — X — chlorine --) (OCH3), For a bromine, iodine, and n, the integer of 1-20 and m are the integer of 0-20.
o, m, p-XCH2-C6H4- 2Si (CH2) 3, o and m, p-CH3C (OCH3) (H) (X) -C6H4- 2Si (CH2) 3, o and m, p-CH3CH2C (OCH3) (H) (X) -C6H4- 2Si (CH2) 3, o and m, p-XCH2-C6H4- (OCH3) 3Si (CH2) 3, o and m, p-CH3C (OCH3) (H) (X) -C6H4- 3Si (CH2) 3, o and m, p-CH3CH2C (OCH3) (H) (X) -C6H4- 3Si (CH2) 3, o and m, p-XCH2-C6H4- (OCH3) 2-O- (CH2) 3Si (CH2) 3, o and m, p-CH3C (OCH3) (H) (X) -C6H4- 2-O- (CH2) 3Si (CH2) 3, o and m, p-CH3CH2C (OCH3) (H) (X) -C6H4- 2-O- (CH2) 3Si (CH2) 3, o and m, p-XCH2-C6H4-O- (OCH3) 3Si (CH2) 3, o and m, p-CH3C (OCH3) (H) (X) -C6H4-O- 3Si (CH2) 3, o and m, p-CH3CH2C (OCH3) (H) (X) -C6H4-O-3-Si (CH2) 3, o and m, p-XCH2-C6H4-O- (OCH3) 2-O- (CH2) 3-Si (CH2)